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[54] **SILICA REINFORCED RUBBER
COMPOSITION AND TIRE WITH TREAD
THEREOF**

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330, 381; 152/209 R**

[56] **References Cited**

U.S. PATENT DOCUMENTS

4,996,260 2/1991 O'Connell 524/381

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[57] **ABSTRACT**

The present invention relates to a rubber composition containing silica reinforcement and to pneumatic tires having treads comprised of such rubber composition.

A rubber composition comprises at least one elastomer, silica, carbon black and a silica coupler comprised of poly-(2-propanol-1,3-polysulfide).

18 Claims, No Drawings

SILICA REINFORCED RUBBER COMPOSITION AND TIRE WITH TREAD THEREOF

FIELD

This invention relates to rubber compositions which contain silica reinforcement and to tires having treads thereof. In one aspect, the rubber composition is comprised of rubber, particularly sulfur cured rubber, reinforced with a combination of silica, and optionally carbon black, and a poly-(2-propanol-1,3-polysulfide) coupling agent.

BACKGROUND

For various applications utilizing rubber which requires high strength and abrasion resistance, particularly applications such as tires and various industrial products, sulfur cured rubber is utilized which contains substantial amounts of reinforcing fillers, often in a range of about 35 to about 85 parts by weight per 100 parts rubber. Carbon black is commonly used for such purpose and normally provides or enhances good physical properties for the sulfur cured rubber. Particulate silica is also often used for such purpose, particularly when the silica is used in conjunction with a coupling agent. In some cases, a combination of silica and carbon black is utilized for reinforcing fillers for various rubber products, including treads for tires. The use of such reinforcing fillers for elastomers, including sulfur curable elastomers, is well known to those skilled in such art.

It is important to appreciate that, conventionally, carbon black is a considerably more effective reinforcing filler for rubber products, and particularly for rubber tire treads than silica if the silica is used without a coupling agent, or silica coupler or silica adhesion agent as it may be sometimes referred to herein.

Such coupling agents may, for example, be premixed, or pre-reacted, with the silica particles or added to the rubber mix during a rubber/silica processing, or mixing, stage. If the coupling agent and silica are added separately to the rubber mix during the rubber/silica mixing, or processing stage, it is considered that the coupling agent then combines in situ with the silica.

In particular, such coupling agents are sometimes composed of a silane which has a constituent component, or moiety, (the silane portion) capable of reacting with the silica surface and, also, a constituent component, or moiety, capable of reacting with the rubber, particularly a sulfur vulcanizable rubber which contains carbon-to-carbon double bonds, or unsaturation. In this manner, then the coupler acts as a connecting bridge between the silica and the rubber and thereby enhances the rubber reinforcement aspect of the silica.

In one aspect, the silane of the coupling agent apparently forms a bond to the silica surface and the rubber reactive component of the coupling agent combines with the rubber itself. Usually the rubber reactive component of the coupler is temperature sensitive and tends to combine with the rubber during the final and higher temperature sulfur vulcanization stage and, thus, subsequent to the rubber/silica/coupler mixing stage and, therefore, after the silane group of the coupler has combined with the silica. However, partly because of typical temperature sensitivity of the coupler, some degree of combination, or bonding, may occur between the rubber-reactive component of the coupler and the rubber during initial rubber/silica/coupler mixing stage(s) and, thus, prior to a subsequent vulcanization stage.

The rubber-reactive group component of the coupler may be, for example, one or more of groups such as mercapto, amino, vinyl, epoxy, and sulfur groups, and is often a sulfur or mercapto moiety and more usually sulfur.

Numerous coupling agents are taught for use in combining silica and rubber, such as, for example, silane coupling agents containing a polysulfide component, or structure, such as, for example, trialkoxyorganosilane polysulfides containing from 2 to 8 sulfur atoms in a polysulfide bridge such as, for example, bis-(3-triethoxysilylpropyl)tetrasulfide and/or trisulfide.

Various U.S. patents relating to silicas and silica reinforced tire treads include, for example, U.S. Pat. Nos. 3,451,458; 3,664,403; 3,768,537; 3,884,285; 3,938,574; 4,482,663; 4,590,052; 5,089,554 and British 1,424,503.

The term "phr" if used herein, and according to conventional practice, refers to "parts of a respective material per 100 parts by weight of rubber, or elastomer".

In the description of this invention, the terms "rubber" and "elastomer" if used herein, may be used interchangeably, unless otherwise prescribed. The terms "rubber composition", "compounded rubber" and "rubber compound", if used herein, are used interchangeably to refer to "rubber which has been blended or mixed with various ingredients and materials" and such terms are well known to those having skill in the rubber mixing or rubber compounding art.

A reference to an elastomer's T_g refers to its glass transition temperature, which can conveniently be determined by a differential scanning calorimeter at a heating rate of 10° C. per minute.

SUMMARY AND PRACTICE OF THE INVENTION

In accordance with one aspect of this invention, a rubber composition is provided which comprises (A) 100 parts by weight of at least one diene-based elastomer, (B) about 25 to about 100, optionally about 35 to about 90, phr of reinforcing filler composed of silica and carbon black, and (C) a silica coupler selected from (i) poly-(2-propanol-1,3-polysulfide) having from 2 to 6 sulfur atoms in its polysulfide bridge or (ii) a combination of about 95 to about 25, alternatively about 90 to about 55, weight percent said poly-(2-propanol-1,3-polysulfide) and, correspondingly, about 5 to about 75, alternatively about 10 to about 45, weight percent of bis-(3-trialkoxysilylalkyl) polysulfide containing from 2 to 8 sulfur atoms in the polysulfide bridge such as, for example, at least one of bis-(3-triethoxysilylpropyl)tetrasulfide and bis-(3-triethoxysilylpropyl)trisulfide; wherein the weight ratio of silica to carbon black is at least 0.1/1, alternatively at least 3/1 and optionally at least 10/1.

Typically, it is desired that the weight ratio of said silica coupler to silica is in a range of about 0.01 to about 0.2/1.

In one aspect of the invention, such a rubber composition is provided wherein said reinforcing filler is composed of about 25 to about 90 phr of silica and up to about 30 phr carbon black.

In one aspect of the invention, the silica coupler is composed of about 90 to about 55 weight percent poly-(2-propanol-1,3-polysulfide) and correspondingly, about 10 to about 45 weight percent of at least one of bis-(3-triethoxysilylpropyl) tetrasulfide and bis-(3-triethoxysilylpropyl) trisulfide.

In the practice of this invention, a ratio of silica to carbon black may be used in a range of about 3/1 to about 30/1.

Thus, in one aspect of the invention, the rubber composition contains a combination of both silica and carbon black as elastomer reinforcing pigments.

The rubber composition may contain a minor amount of silica in its silica/carbon black or it may be quantitatively reinforced with silica where carbon black is present in a minor amount.

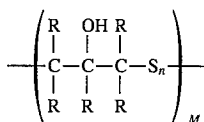
In another aspect of the invention, a tire is provided having a tread comprised of the said rubber composition of this invention.

Typically, it is desired that the weight ratio of said silica coupler to silica is in a range of about 0.01/1 to about 0.2/1.

In one aspect, the precipitated silica is usually characterized by having a BET surface area in a range of about 50 to about 300 square meters per gram and a dibutylphthalate (DBP) absorption value in a range of about 150 to about 300.

The said poly-(2-propanol-1,3-polysulfide) silica coupler may more fully be described as a polymeric secondary alcohol with polysulfide linkages on the 1 and 3 carbon atom positions. By the 1 and 3 carbon atom positions, it is meant the terminal carbons, or terminal methylenes of 2-propanol, that are attached to the polysulfide bridges. By the term "polymeric" secondary alcohol, it is meant that repeat units of 2-propanol are connected by repeat polysulfide bridges attached to the 1 and 3 positions of 2-propanol.

A representative formula for such polymeric polysulfide is as follows:



where R is hydrogen or alkyl radical. For example, R may be the same or different and selected from hydrogen, methyl, ethyl, n-propyl, isopropyl, n-butyl, etc. radicals.

M is representative of the number of repeating units in the polymeric polysulfide and is an integer ranging from about 3 to about 250, and n represents the number of sulfur atoms in the polysulfidic bridge and is 2 to about 6.

It is believed that the poly-(2-propanol-1,3-polysulfide) acts to associate strongly to the silica surface through secondary alcohol groups of the polymeric coupler and, thus, couple the silica to the diene polymer by attachment of the rubber reactive polysulfide portion of the coupler. This is considered herein to be beneficial as enabling the silica coupling to the polymer through relatively strong ionic bonds.

Where it is desired that the rubber composition is primarily reinforced with silica as the reinforcing pigment, it is preferable that the weight ratio of silica to carbon black is at least 3/1, alternatively at least 10/1 and, thus, for example, in a range of about 3/1 to about 30/1.

In one aspect of the invention, the silica coupler consists essentially of the poly-(2-propanol-1,3-polysulfide).

In a further aspect, the silica coupler can be composed of a combination of the poly-(2-propanol-1,3-polysulfide) together with bis-(3-triethoxysilylpropyl)tetrasulfide and/or a blend of such tetrasulfide and bis-(3-triethoxysilylpropyl) trisulfide.

The poly-(2-propanol-1,3-polysulfide) can also be referred to as a poly secondary alcohol tetrasulfide of varied chain lengths and molecular weights. While it is referred to herein as a polysulfide, it typically contains an average of

about 3.5 to about 4.5 sulfur atoms in its polysulfidic moiety. In one aspect, it can also be referred to as a non-silane silica-to-rubber coupler. In particular, it can be characterized by having the properties of a melting point in a range of about 90° C. to about 118° C.; and infrared spectrometric secondary alcohol absorption bond intensity in a range of about 3570 cm⁻¹ to about 3450 cm⁻¹ and about 1100 cm⁻¹ and 1350 cm⁻¹ to about 1260 cm⁻¹. Small molecule GPC analysis shows a high molecular weight in the region of 18,000–20,000, with about 60–96 percent of its molecular weight greater than 9000.

The poly-(2-propanol-1,3-polysulfide) is considered herein to be particularly advantageous for the practice of this invention because it has a very strong associative attraction to silica and high reactivity for rubber which is considered to be a benefit to the exceptionally good dispersion of silica into the rubber.

Historically, the more homogeneous the dispersion of rubber compound components into the rubber, the better the resultant cured properties of that rubber. The poly-(2-propanol-1,3-polysulfide)'s strong association to silica and high affinity, compatibility, and reactivity with rubber is considered herein to lead to excellent silica dispersion within the elastomer composition.

In one aspect, such a rubber composition can be provided as being sulfur cured. The sulfur curing is accomplished in a conventional manner, namely, by curing under conditions of elevated temperature and pressure for a suitable period of time.

In the practice of this invention, as hereinbefore pointed out, the rubber composition is comprised of at least one diene-based elastomer, or rubber; thus, it is considered that the elastomer is a sulfur curable elastomer. Such elastomer, or rubber, may be selected, for example, from at least one of cis 1,4-polyisoprene rubber (natural and/or synthetic, and preferably natural rubber), 3,4-polyisoprene rubber, styrene/butadiene copolymer rubbers, styrene/isoprene/butadiene terpolymer rubbers, and cis 1,4-polybutadiene rubber.

In one aspect the rubber is preferably of at least two diene based rubbers. Such diene based rubbers may, for example, be of homopolymers and copolymers of conjugated diene hydrocarbons and copolymers of at least one diene hydrocarbon with a vinyl aromatic compound. Such diene hydrocarbons may be, for example, selected from 1,3-butadiene and isoprene. Such vinyl aromatic compound may be, for example, styrene or alphas-methylstyrene. For example, a combination of two or more rubbers is preferred such as at least elastomers selected from cis 1,4-polyisoprene rubber (natural or synthetic, although natural is preferred), 3,4-polyisoprene rubber, isoprene/butadiene rubber, styrene/isoprene/butadiene rubber, emulsion and solution polymerization derived styrene/butadiene rubbers, cis 1,4-polybutadiene rubber, medium vinyl polybutadiene rubber having a vinyl content of from 30 to 50, high vinyl polybutadiene having a vinyl content of from 50 to 75, and emulsion polymerization prepared butadiene/acrylonitrile copolymers.

In one aspect of this invention, an emulsion polymerization derived styrene/butadiene (E-SBR) might be used having a relatively conventional styrene content of about 20 to about 28 percent bound styrene or, for some applications, an E-SBR having a medium to relatively high bound styrene content, namely, a bound styrene content of about 30 to about 45 percent.

The relatively high styrene content of about 30 to about 45 for the E-SBR can be considered beneficial for a purpose of

enhancing traction, or skid resistance, of the tire tread. The presence of the E-SBR itself is considered beneficial for a purpose of enhancing processability of the uncured elastomer composition mixture, especially in comparison to a utilization of a solution polymerization prepared SBR (S-SBR).

By emulsion polymerization prepared E-SBR, it is meant that styrene and 1,3-butadiene are copolymerized as an aqueous emulsion. Such are well known to those skilled in such art. The bound styrene content can vary, for example, from about 5 to 50%. In one aspect, the E-SBR may also contain acrylonitrile to form a terpolymer rubber, as E-SBAR, in amounts, for example, of about 2 to about 30 weight percent bound acrylonitrile in the terpolymer.

Emulsion polymerization prepared styrene/butadiene/acrylonitrile copolymer rubbers containing about 2 to about 40 weight percent bound acrylonitrile in the copolymer are also contemplated as diene based rubbers for use in this invention.

The solution polymerization prepared SBR (S-SBR) typically has a bound styrene content in a range of about 5 to about 50, preferably about 9 to about 36, percent. The S-SBR can be conveniently prepared, for example, by organo lithium catalyzed polymerization in the presence of an organic hydrocarbon solvent.

A purpose of using S-SBR is for improved tire rolling resistance as a result of lower hysteresis when it is used in a tire tread composition.

The 3,4-polyisoprene rubber (3,4-PI) is considered beneficial for a purpose of enhancing the tire's traction when it is used in a tire tread composition.

The 3,4-PI and use thereof is more fully described in U.S. Pat. No. 5,087,668 which is incorporated herein by reference. The T_g refers to the glass transition temperature which can conveniently be determined by a differential scanning calorimeter at a heating rate of 10° C. per minute.

The cis 1,4-polybutadiene rubber (BR) is considered to be beneficial for a purpose of enhancing the tire tread's wear, or treadwear.

Such BR can be prepared, for example, by organic solution polymerization of 1,3-butadiene.

The BR may be conveniently characterized, for example, by having at least a 90% cis 1,4-content.

The cis 1,4-polyisoprene and cis 1,4-polyisoprene natural rubber are well known to those having skill in the rubber art.

The vulcanized rubber composition should contain a sufficient amount of silica, and carbon black reinforcing filler(s) to contribute a reasonably high modulus and high resistance to tear. The combined weight of the silica and carbon black, as hereinbefore referenced, may be as low as about 30 parts per 100 parts rubber, but is preferably from about 35 or 45 to about 90 parts by weight.

The commonly employed siliceous pigments used in rubber compounding applications can be used as the silica in this invention, including pyrogenic and precipitated siliceous pigments (silica), although precipitate silicas are preferred.

The siliceous pigments preferably employed in this invention are precipitated silicas such as, for example, those obtained by the acidification of a soluble silicate, e.g., sodium silicate.

Such silicas might be characterized, for example, by having a BET surface area, as measured using nitrogen gas, preferably in the range of about 40 to about 600, and more usually in a range of about 50 to about 300 square meters per

gram. The BET method of measuring surface area is described in the *Journal of the American Chemical Society*, Volume 60, page 304 (1930).

The silica may also be typically characterized by having a dibutylphthalate (DBP) absorption value in a range of about 100 to about 400, and more usually about 150 to about 300.

The silica might be expected to have an average ultimate particle size, for example, in the range of 0.01 to 0.05 micron as determined by the electron microscope, although the silica particles may be even smaller, or possibly larger, in size.

Various commercially available silicas may be considered for use in this invention such as, only for example herein, and without limitation, silicas commercially available from PPG Industries under the Hi-Sil trademark with designations 210, 243, etc.; silicas available from Rhone-Poulenc, with, for example, Zeosil 1165MP and silicas available from Degussa AG with, for example, designations VN2 and VN3, etc.

It is readily understood by those having skill in the art that the rubber composition would be compounded by methods generally known in the rubber compounding art, such as mixing the various sulfur-vulcanizable constituent rubbers with various commonly used additive materials such as, for example, curing aids, such as sulfur, activators, retarders and accelerators, processing additives, such as oils, resins including tackifying resins, silicas, and plasticizers, fillers, pigments, fatty acid, zinc oxide, waxes, antioxidants and antiozonants, peptizing agents and reinforcing materials such as, for example, carbon black. As known to those skilled in the art, depending on the intended use of the sulfur vulcanizable and sulfur vulcanized material (rubbers), the additives mentioned above are selected and commonly used in conventional amounts.

Typical amounts of reinforcing type carbon blacks(s), for this invention, if used, are hereinbefore set forth. It is to be appreciated that the silica coupler may be used in conjunction with a carbon black, namely, pre-mixed with a carbon black prior to addition to the rubber composition, and such carbon black is to be included in the aforesaid amount of carbon black for the rubber composition formulation. Typical amounts of tackifier resins, if used, comprise about 0.5 to about 10 phr, usually about 1 to about 5 phr. Typical amounts of processing aids comprise about 1 to about 50 phr. Such processing aids can include, for example, aromatic, naphthenic, and/or paraffinic processing oils. Typical amounts of antioxidants comprise about 1 to about 5 phr. Representative antioxidants may be, for example, diphenyl-p-phenylenediamine and others, such as, for example, those disclosed in the *Vanderbilt Rubber Handbook* (1978), pages 344-346. Typical amounts of antiozonants comprise about 1 to 5 phr. Typical amounts of fatty acids, if used, which can include stearic acid comprise about 0.5 to about 3 phr. Typical amounts of zinc oxide comprise about 2 to about 5 phr. Typical amounts of waxes comprise about 1 to about 5 phr. Often microcrystalline waxes are used. Typical amounts of peptizers comprise about 0.1 to about 1 phr. Typical peptizers may be, for example, pentachlorothiophenol and dibenzamidodiphenyl disulfide.

The vulcanization is conducted in the presence of a sulfur vulcanizing agent. Examples of suitable sulfur vulcanizing agents include elemental sulfur (free sulfur) or sulfur donating vulcanizing agents, for example, an amine disulfide, polymeric polysulfide or sulfur olefin adducts. Preferably, the sulfur vulcanizing agent is elemental sulfur. As known to

those skilled in the art, sulfur vulcanizing agents are used in an amount ranging from about 0.5 to about 4 phr, or even, in some circumstances, up to about 8 phr, with a range of from about 1.5 to about 2.5, sometimes from 2 to 2.5, being preferred.

Accelerators are used to control the time and/or temperature required for vulcanization and to improve the properties of the vulcanizate. In one embodiment, a single accelerator system may be used, i.e., primary accelerator. Conventionally and preferably, a primary accelerator(s) is used in total amounts ranging from about 0.5 to about 4, preferably about 0.8 to about 1.5, phr. In another embodiment, combinations of a primary and a secondary accelerator might be used with the secondary accelerator being used in smaller amounts (of about 0.05 to about 3 phr) in order to activate and to improve the properties of the vulcanizate. Combinations of these accelerators might be expected to produce a synergistic effect on the final properties and are somewhat better than those produced by use of either accelerator alone. In addition, delayed action accelerators may be used which are not affected by normal processing temperatures but produce a satisfactory cure at ordinary vulcanization temperatures. Vulcanization retarders might also be used. Suitable types of accelerators that may be used in the present invention are amines, disulfides, guanidines, thioureas, thiazoles, thiurams, sulfenamides, dithiocarbamates and xanthates. Preferably, the primary accelerator is a sulfenamide. If a second accelerator is used, the secondary accelerator is preferably a guanidine, dithiocarbamate or thiuram compound. The presence and relative amounts of sulfur vulcanizing agent and accelerator(s) are not considered to be an aspect of this invention which is more primarily directed to the use of silica as a reinforcing filler in combination with poly-(2-propanol-1,3-polysulfide) as a coupling agent.

The presence and relative amounts of the above additives are not considered to be an aspect of the present invention which is more primarily directed to the utilization of specified blends of rubbers in rubber compositions, in combination with silica and with poly-(2-propanol-1,3-polysulfide) individually or in combination with bis-(3-triethoxysilylpropyl) tetrasulfide as well as, optionally, carbon black, for the reinforcement of the rubber.

The mixing of the rubber composition can be accomplished by methods known to those having skill in the rubber mixing art. For example, the ingredients are typically mixed in at least two stages, namely, at least one non-productive stage followed by a productive mix stage. The final curatives are typically mixed in the final stage which is conventionally called the "productive" mix stage in which the mixing typically occurs at a temperature, or ultimate temperature, lower than the mix temperature(s) than the preceding non-productive mix stage(s). The rubber, silica and silica coupler, and carbon black if used, are mixed in one or more nonproductive mix stages. The terms "non-productive" and "productive" mix stages are well known to those having skill in the rubber mixing art.

The rubber composition of this invention can be used for various purposes. For example, it can be used for various tire compounds. Such tires can be built, shaped, molded and cured by various methods which are known and will be readily apparent to those having skill in such art.

The invention may be better understood by reference to the following examples in which the parts and percentages are by weight unless otherwise indicated.

EXAMPLE I

Poly(2-propanol-1,3-polysulfide) is prepared as follows:

A 2-liter, 3-neck resin flask was charged with 129.6g (0.54 mole) of sodium sulfide nonahydrate and 51.8 g (1.62

moles) of sulfur and 400 ml of distilled water. The flask was purged with nitrogen gas and sealed under a nitrogen balloon. The flask was heated to 95° C. with stirring and the formation of the clear red-colored tetrasulfide dianion was observed. Neat (1.08 moles) epichlorohydrin (100 g) was added very slowly in a dropwise manner as to control the highly exothermic nature of the reaction.

After about ¾ hour addition time, a rubbery polymeric ball forms on the stirrer blade and the red color is discharged. The polymeric material is removed from the flask and analyzed by FTIR analysis, which shows disappearance of the chloro and epoxide functional groups and formation of the hydroxyl group. The term "FTIR analysis" refers to "Fourier Transform Infrared spectroscopic analysis".

Small molecule GPC shows a repeat oligomeric pattern up to about 20,000 molecular weight, with 35.9% of the polymer molecular weight in the 19,330 mw region; 38.7% in the 9940 mw region; 1.8% in the 840 mw region; 201% in the 720 mw region; 2.4% in the 610 mw region; 2.9% in the 510 mw region; 2.8% in the 390 mw region and 2.5% in the 270 mw region. The term "GPC" refers to gel permeation chromatography.

The polymer was cut into about ¾-inch cubes for compounding with an elastomer composition. The polymer is observed to flow at 118° C. and weighs 175 g after drying at 70° C. under 29 inches of mercury vacuum for 4 hours.

EXAMPLE II

Poly(2-propanol-1,3-disulfide) is prepared as follows:

A reaction was carried out under the conditions of Example I except that the resin flask was charged with 129.6g (0.54 mole) of the sodium sulfide nonohydrate and 17.3g (0.54 mole) of sulfur in 400 mls of distilled water to form the polysulfide mixture.

Work-up and vacuum drying gave 69 g of polymer which was observed to flow at 88° C. and evidences a small molecule GPC distribution with 30.8% in the 19,330 region; 33.3% in the 9940 mw region; 1.5% in the 840 mw region; 1.8% in the 720 mw region; 2.0% in the 610 mw region; 2.4% in the 510 mw region and 20.5% in the 270 mw region.

EXAMPLE III

Poly(2-propanol-1,3-hexasulfide) is prepared as follows:

A reaction was carried out under the conditions of Example I except that the resin flask was charged with 129.g (0.54 mole) of the sodium sulfide nonahydrate and 86.4g (2.7 moles) of sulfur in 500 ml of distilled water to form the polysulfide mixture.

Work-up and vacuum drying gave 139 g of polymer which was observed to flow at 68° C. and evidences a small molecule GPC distribution with 44.9% of the polymer molecular weight in the 19,330 region; 47.7% in the 9940 region and 5.5% in the 840 mw region.

One can readily recognize that the ratio of epichlorohydrin to the polysulfide in Examples I, II and III can be changed as desired to adjust the ratio of alkanol to sulfur in the final product.

EXAMPLE IV

In this Example, poly-(2-propanol-1,3tetrasulfide), prepared according to Example I, was evaluated as an alternative for a relatively commonly used silica to elastomer coupling agent, namely, bis(3-triethoxysilylpropyl) tetrasulfide

fide, on a carbon black as a carrier, in a silica reinforced rubber composition.

Rubber compositions containing the materials set out in Table 1 were prepared in a BR Banbury rubber mixer using three separate, sequential stages of addition (mixing), namely, two non-productive mix stages and one final productive mix to temperatures of 160° C., 160° C. and 120° C. and times of 4 minutes, 4 minutes and 2 minutes, respectively. The amount of coupler is listed as being "variable" in Table 1 and is more specifically set forth in Table 2.

Sample 1 is considered herein as a control without using a silica-to-elastomer coupling agent.

It is clearly evident that utilization of the coupling agent (Samples 2 and 3) appears to be necessary to obtain suitable cured properties in a silica containing rubber composition, or compound. Such properties include, for example, tensile strength at break, the 100 and 300% modulus values, rebound hardness, Rheovibron E' and particularly DIN abrasion resistance (lower indicate less, or values better, abrasion values).

Samples 2 and 3, when compared to Sample 1 which was prepared in the absence of utilization of the silica coupling agent, clearly show the advantage of the coupling agents. The properties of Sample 3, which contains the silica coupler utilized in this invention has properties at least equivalent or somewhat better than those exhibited by Sample 2 which contains the aforesaid conventional silane coupling agent.

In particular, this Example shows that the poly(2-propanol-1,3-tetrasulfide), as utilized in Sample 3, can provide significant improvements in modulus, rebound, hardness and abrasion when compared to control Sample 1 which does not contain a silica to elastomer coupling agent. Furthermore, these properties compare favorably to those of Sample 2 which contains the conventional silane coupling agent.

TABLE 1

1st Non-Productive	
Cis 1,4-Polyisoprene ¹ Rubber	100.00
Carbon Black	35.00
Processing Oil	5.00
Zinc Oxide	5.00
Fatty Acid	2.00
Antioxidant ²	2.00
2nd Non-Productive	
Silica ³	15.00
Bis-(3-triethoxysilylpropyl) tetrasulfide ⁴	variable
Poly-(2-propanol-1,3-tetrasulfide) ⁵	variable
Productive	
Sulfur	1.40
Accelerator, sulfenamide type	1.00

¹synthetic cis 1,4-polyisoprene rubber (NAT 2200) from The Goodyear Tire & Rubber Company;

²of the polymerized 1,2-dihydro-2,2,4-trimethylquinoline type;

³silica obtained as Hi-Sil-210 from PPG Industries, Inc.;

⁴50% active composite composed of the organosilane tetrasulfide on or with carbon black in a 50/50 weight ratio available as material X50S from Degussa GmbH. Technically the organosilane polysulfide is understood to be a composite, or mixture, in which the average polysulfide bridge contains about 3.5 to 4 connecting sulfur atoms, although the mixture may contain such polysulfides with about 2 to 8 connecting sulfur atoms; and

⁵reaction product produced in Example I herein.

TABLE 2

	Sample #		
	1	2	3
X50S (Degussa GmbH)	0	3	0
Poly-(2-propanol-1,3-tetrasulfide)	0	0	2
Rheometer (150° C.)			
Max. Torque, dNm	30.2	34.3	36.5
Min. Torque, dNm	7.0	7.0	7.5
Delta Torque	23.2	27.3	29.0
T ₉₀ , minutes	23.0	18.7	15.7
Stress-Strain			
Tensile Strength, MPa	17.6	19.7	20.4
Elongation at Break, %	630	621	620
100% Modulus, MPa	1.2	1.7	1.8
300% Modulus, MPa	5.5	8.0	7.7
Rebound			
100° C., %	55.1	59.8	61.0
Hardness			
Shore A, 100° C.	46.4	51.9	54.6
Rheovibron			
E' at 60° C., MPa	10.6	11.5	14.8
Tan Delta at 60°	.105	.092	.085
DIN Abrasion	231	156	154

EXAMPLE V

In this Example, poly-(2-propanol-1,3-tetrasulfide), prepared according to Example I, was evaluated as an alternative for a relatively commonly used silica coupling agent, bis-(3-triethoxysilylpropyl) tetrasulfide, on a carbon black as a carrier, in a silica reinforced rubber composition.

The rubber compositions containing the materials set out in Table 3 were prepared in a BR Banbury rubber mixer using three separate, sequential stages of addition (mixing), namely, two non-productive mix stages and one final productive mix to temperatures of 160° C., 160° C. and 120° C. and times of 4 minutes, 4 minutes and 2 minutes, respectively. The amount of coupler is listed as being "variable" in Table 3 and is more specifically set forth in Table 4.

It is clearly evident that utilization of coupling agent appears to be necessary to obtain suitable cured properties in a silica containing rubber composition, or compound. Such properties include tensile strength at break, the 100 and 300% modulus values, rebound hardness, Rheovibron E' and particularly DIN abrasion resistance (lower indicate less, or values better, abrasion values). Samples 5 and 6, when compared to Sample 4, which was prepared in the absence of utilization of the silica coupling agent, clearly show the advantage of the coupling agents. The properties of Sample 6, which contains the silica coupler utilized in this invention has properties better than those exhibited by Sample 4 which has no coupling agent present.

In particular, this Example shows that the poly(2-propanol-1,3-tetrasulfide), as utilized in Sample 6, can provide significant improvements in modulus, rebound, hardness and abrasion when compared to control Sample 4 which does not contain coupling agent.

TABLE 3

1st Non-Productive	
Cis 1,4-Polyisoprene ¹ Rubber	100.00
Carbon Black	15.00
Silica ³	20.00
Processing Oil	5.00
Zinc Oxide	5.00
Fatty Acid	2.00
Antioxidant ²	2.00
2nd Non-Productive	
Silica ³	15.00
Bis-(3-triethoxysilylpropyl) tetrasulfide ⁴	variable
Poly-(2-propanol-1,3-tetrasulfide) ⁵	variable
Productive	
Sulfur	1.50
Accelerator, sulfenamide type	2.00
Accelerator, diphenylguanidine	0.50

¹synthetic cis 1,4-polyisoprene rubber (NAT 2200) from The Goodyear Tire & Rubber Company;
²of the polymerized 1,2-dihydro-2,2,4-trimethylquinoline type;
³silica obtained as Hi-Sil-210 from PPG Industries, Inc.;
⁴50% active composite composed of the organosilane tetrasulfide on or with carbon black in a 50/50 weight ratio available as material X50S from Degussa GmbH. Technically the organosilane polysulfide is understood to be a composite, or mixture, in which the average polysulfide bridge contains about 3.5 to 4 connecting sulfur atoms, although the mixture may contain such polysulfides with about 2 to 8 connecting sulfur atoms; and
⁵Poly-(2-propanol)-1,3-tetrasulfide, obtained as the reaction product produced in Example I herein.

TABLE 4

	Sample #		
	4	5	6
X50S (Degussa GmbH)	0	5	0
Poly-(2-propanol-1,3-tetrasulfide)	0	0	3
Rheometer (150° C.)			
Max. Torque, dNm	39.2	43.0	43.0
Min. Torque, dNm	9.0	7.0	8.0
Delta Torque	30.0	36.0	35.0
T ₉₀ , minutes	18.8	16.3	14.0
Stress-Strain			
Tensile Strength, MPa	18.6	22.3	21.2
Elongation at Break, %	706	568	593
100% Modulus, MPa	1.3	2.6	2.4
300% Modulus, MPa	4.4	11.1	9.1
Rebound			
100° C., %	60.1	67.8	66.5
Hardness			
Shore A, 100° C.	55.6	64.3	64.2
Rheovibron			
E' at 60° C., MPa	14.1	19.7	23.1
Tan Delta at 60°	.076	.056	.050
DIN Abrasion	270	125	157

EXAMPLE VI

In this Example, the poly-(2-propanol-1,3-tetrasulfide) was evaluated in a highly silica loaded rubber composition. Rubber compositions containing the materials set out in Table 5 were prepared in a BR Banbury mixer using three separate stages of addition, namely, two non-productive mix stages and one productive mix stage to temperatures of 160°

C., 160° C. and 120° C. and times of 4 minutes, 4 minutes and 2 minutes, respectively. The cure behavior and cured properties are indicated in Table 6.

The combination of the poly-(2-propanol-1,3-tetrasulfide) and the conventional coupling agent gave a rubber composition exhibiting excellent cured properties in the presence of high levels of silica filler.

TABLE 5

1st Non-Productive	
Styrene/Butadiene Rubber ¹	68.75
Cis 1,4-Polybutadiene ² Rubber	15.00
Cis 1,4-Polyisoprene ³ Rubber	35.00
Carbon Black	20.00
Silica ⁴	40.00
Zinc Oxide	3.00
Fatty Acid	3.00
Antioxidant ⁵	2.00
Processing Aid ⁶	5.00
Poly-(2-propanol-1,3-tetrasulfide) ⁷	4.00
2nd Non-Productive	
Silica ⁴	30.00
Bis-(3-triethoxysilylpropyl) tetrasulfide ⁸ (50% active)	3.00
Productive	
Sulfur	1.4
Accelerator, Sulfenamide Type	1.8
Diphenylguanidine	1.5

¹Emulsion polymerization prepared styrene/butadiene copolymer elastomer (SBR 1712) containing 23.5% bound styrene and 37.5 phr aromatic oil from The Goodyear Tire & Rubber Company;
²high cis 1,4-polybutadiene rubber (BUD 1207) from The Goodyear Tire & Rubber Company;
³synthetic cis 1,4-polyisoprene rubber (NAT 2200) from The Goodyear Tire & Rubber Company;
⁴Zeosil 1165 MP from Rhone-Poulenc;
⁵polymerized 1,2-hydro-2,2,4-trimethylquinoline type;
⁶Struktol A6;
⁷reaction product of Example I herein; and
⁸X50S, from Degussa GmbH.

TABLE 6

	Sample #
	7
<u>Rheometer, 150° C.</u>	
Max. Torque, dNm	53.3
Min. Torque, dNm	10.3
Delta Torque	43.0
T ₉₀ , minutes	17.5
<u>Stress-Strain</u>	
Tensile Strength, MPa	12.7
Elongation at Break, %	340
100% Modulus, MPa	3.72
300% Modulus, MPa	7.98
<u>Rebound</u>	
100° C., %	58.0
<u>Hardness</u>	
Shore A, 100° C.	68.4
<u>Rheovibron</u>	
E' at 60°	42.6
Tan. Delta at 60° C.	.075
DIN Abrasion	142

EXAMPLE VII

In this Example, three variations of poly-(2-propanol-1, 3-polysulfide) were evaluated as partial replacements for the

bis-(3-triethoxysilylpropyl) tetrasulfide in a highly silica loaded rubber composition. Rubber compositions containing the materials set out in Table 7 were prepared in a BR Banbury mixer using three separate stages of addition, namely, two non-productive mix stages and one productive mix stage to temperatures of 160° C., 160° C. and 120° C. and times of 4 minutes, 4 minutes and 2 minutes, respectively. The cure behavior and cured properties are indicated in Table 8.

The combination of the poly-(2-propanol-1,3-polysulfide) of this invention and the conventional coupling agent gave a rubber composition exhibiting excellent cured properties in the presence of high levels of silica filler.

TABLE 7

1st Non-Productive	
Styrene/Butadiene Rubber ¹	68.75
Cis 1,4-Polybutadiene Rubber ²	15.00
Cis 1,4-Polyisoprene Rubber ³	35.00
Carbon Black	20.00
Silica ⁴	40.00
Zinc Oxide	3.00
Fatty Acid	3.00
Antioxidant ⁵	2.00
Processing Aid ⁶	5.00
Poly-(2-propanol-1,3-di, tetra, or hexa sulfide) ⁷	0 or 4.00
2nd Non-Productive	
Silica ⁴	30.00
Bis-(3-triethoxysilylpropyl) tetrasulfide ⁸ (50% active)	3.00
Productive	
Sulfur	1.4
Accelerator, Sulfenamide Type	1.8
Diphenylguanidine	1.5

¹Emulsion polymerization prepared styrene/butadiene copolymer elastomer (SBR 1712) containing 23.5% bound styrene and 37.5 phr aromatic oil from The Goodyear Tire & Rubber Company;

²high cis 1,4-polybutadiene rubber (BUD 1207) from The Goodyear Tire & Rubber Company;

³synthetic cis 1,4-polyisoprene rubber (NAT 2200) from The Goodyear Tire & Rubber Company;

⁴Zeosil 1165 MP from Rhone-Poulenc;

⁵polymerized 1,2-hydro-2,2,4-trimethylquinoline type;

⁶Struktol A6;

⁷reaction products of Examples I, II and III herein, respectively; and

⁸X50S, from Degussa GmbH.

TABLE 8

	Sample #			
	8	9	10	11
X50S	0	3	3	3
Disulfide	0	4	0	0
from Ex. II				
Tetrasulfide	0	0	4	0
from Ex. I				
Hexasulfide	0	0	0	4
from Ex. III				
Rheometer, 150° C.				
Max. Torque, dNm	43.0	50.0	55.5	61.5
Min. Torque, dNm	14.0	11.0	11.0	13.0
Delta Torque	29.0	39.0	44.5	48.5
T ₉₀ , minutes	20.3	17.5	17.5	15.0
Stress-Strain				
Tensile Strength, MPa	11.5	14.5	13.9	14.2

TABLE 8-continued

	Sample #			
	8	9	10	11
Elongation at Break, %	632	492	378	336
100% Modulus, MPa	1.2	2.8	3.7	4.3
300% Modulus, MPa	4.1	9.8	12.2	13.8
Rebound				
100° C., %	47.5	55.7	59.8	61.1
Hardness				
Shore A, 100° C.	50.6	64.4	68.2	70.0
Rheovibron				
E' at 60° C.	15.7	33.0	38.2	39.5
Tan. Delta at 60° C.	.116	.086	.074	.064
DIN Abrasion	226	147	150	150

While certain representative embodiments and details have been shown for the purpose of illustrating the invention, it will be apparent to those skilled in this art that various changes and modifications may be made therein without departing from the spirit or scope of the invention.

What is claimed is:

1. A rubber composition comprised of (A) 100 parts by weight of at least one diene-based elastomer, (B) about 25 to about 100 phr of filler composed of particulate, precipitated silica and carbon black, and (C) a silica coupler selected from (i) poly-(2-propanol-1,3-polysulfide), having from 2 to 6 sulfur atoms in its polysulfide bridge, or from (ii) a combination of about 95 to about 25 weight percent of said poly-(2-propanol-1,3-polysulfide) and, correspondingly, about 5 to about 75 weight percent of bis-(3-trialkoxysilylalkyl) polysulfide containing from 2 to 8 sulfur atoms in its polysulfide bridge; wherein the weight ratio of said silica coupler to silica is in a range of about 0.01/1 to about 0.2/1; wherein the weight ratio of silica to carbon black, is at least about 0.1/1.

2. The rubber composition of claim 1 where said poly-(2-propanol-1,3-polysulfide) is on a carbon black carrier.

3. The rubber composition of claim 1 wherein the said silica coupler consists essentially of poly(2-propanol-1,3-polysulfide); and wherein the weight ratio of said silica coupler to silica is in a range of about 0.01/1 to about 0.2/1.

4. The rubber composition of claim 1 wherein the said silica coupler is a combination of about 95 to about 25 weight percent poly-(2-propanol-1,3-polysulfide) and, correspondingly, about 5 to about 75 weight percent of bis-(3-triethoxysilylpropyl) tetrasulfide and bis-(3-triethoxysilylpropyl) trisulfide.

5. The rubber composition of claim 1 wherein the diene based elastomer is selected from at least one of cis 1,4-polyisoprene rubber, 3,4-polyisoprene rubber, styrene/butadiene copolymer rubbers, isoprene/butadiene rubber, styrene/isoprene/butadiene terpolymer rubbers, cis 1,4-polybutadiene rubber, medium vinyl polybutadiene rubber, high vinyl polybutadiene rubber and emulsion polymerization prepared styrene/butadiene/acrylonitrile terpolymer rubber and butadiene/acrylonitrile copolymer rubber.

6. The rubber composition of claim 1 wherein the silica is characterized by having a BET surface area in a range of about 50 to about 300 square meters per gram and a dibutylphthalate (DBP) absorption value in a range of about 150 to about 300.

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7. The rubber composition of claim 2 wherein the silica is characterized by having a BET surface area in a range of about 50 to about 300 square meters per gram and a dibutylphthalate (DBP) absorption value in a range of about 150 to about 300.

8. The rubber composition of claim 3 wherein the silica is characterized by having a BET surface area in a range of about 50 to about 300 square meters per gram and a dibutylphthalate (DBP) absorption value in a range of about 150 to about 300.

9. A rubber composition comprised of (A) 100 parts by weight of at least one diene-based elastomer, (B) about 25 to about 90 phr particulate silica, (C) up to about 30 phr carbon black, and (D) a silica coupler which is collectively composed of about 90 to about 55 weight percent poly-(2-propanol-1,3-polysulfide), about 10 to about 45 weight percent of bis-(3-triethoxysilylpropyl)tetrasulfide and bis-(3-triethoxysilylpropyl)trisulfide; wherein the weight ratio of said silica coupler to silica is in a range of about 0.01/1 to about 0.2/1; wherein the weight ratio of silica to carbon black is in a range of about 3/1 to about 30/1; wherein the silica is characterized by having a BET surface area in a range of about 50 to about 300 square meters per gram and

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a dibutylphthalate (DBP) absorption value in a range of about 150 to about 300.

10. A tire having a rubber tread wherein said tread is comprised of the rubber composition of claim 1.

11. A tire having a rubber tread wherein said tread is comprised of the rubber composition of claim 2.

12. A tire having a rubber tread wherein said tread is comprised of the rubber composition of claim 3.

13. A tire having a rubber tread wherein said tread is comprised of the rubber composition of claim 4.

14. A tire having a rubber tread wherein said tread is comprised of the rubber composition of claim 5.

15. A tire having a rubber tread wherein said tread is comprised of the rubber composition of claim 6.

16. A tire having a rubber tread wherein said tread is comprised of the rubber composition of claim 7.

17. A tire having a rubber tread wherein said tread is comprised of the rubber composition of claim 8.

18. A tire having a rubber tread wherein said tread is comprised of the rubber composition of claim 9.

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